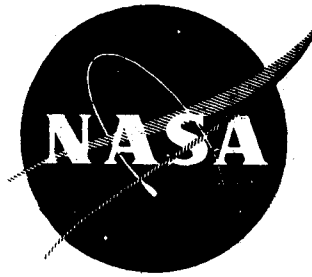


NASA CR 54249



GPO PRICE \$ \_\_\_\_\_

OTS PRICE(S) \$ \_\_\_\_\_

Hard copy (HC) 1.00

Microfiche (MF) .50

FACILITY FORM 502

N65 13846

(ACCESSION NUMBER)

22

(PAGES)

CR 54249

(NASA CR OR TMX OR AD NUMBER)

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(CATEGORY)

STUDY PROGRAM TO IMPROVE FUEL CELL  
PERFORMANCE BY PULSING TECHNIQUES

BY

M. L. KRONENBERG

PREPARED FOR

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

CONTRACT NAS3-6460

UNION CARBIDE CORPORATION

QUARTERLY REPORT

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Quarter Ending November 30, 1964

CONTRACT NAS3-6460

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# STUDY PROGRAM TO IMPROVE FUEL CELL PERFORMANCE BY PULSING TECHNIQUES

by M. L. Kronenberg

## ABSTRACT

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It has been observed under certain conditions that heavy discharge pulses significantly improve the performance level of fuel cells. This investigation is concerned with defining the conditions under which pulsing improves fuel cell performance. How this "pulsing effect" depends on such factors as nature of the catalyst, catalyst concentration and temperature, as well as its effect on electrode life will also be studied.

\* \* \* \* \*

## SUMMARY

*Author*

Pulsing experiments were conducted on smooth Pt, Pd and Rh electrodes and Union Carbide composite electrodes to determine the beneficial pulsing conditions for these electrodes. Hydrogen and oxygen were the anode and cathode gases used. The electrodes were run at steady state currents prior to pulsing at a current density which was sufficient to polarize the working electrode 25 mv or more. The cell was then pulsed and the potential of the working electrode with respect to a mercuric oxide reference electrode was noted before, during, and after pulsing. The potential level attained during the pulse appears to be the most significant factor in determining whether the performance level of the electrode improves as a result of the pulse. The potential ranges (versus NHE) attained during the heavy discharge pulse which resulted in improved performance levels are given in Table I.

TABLE I

### POTENTIAL RANGES (VS. NHE) DURING HEAVY DISCHARGE PULSE

Electrode	Potential Range (vs. NHE) for	
	Anode	Cathode
Solid Pt	-0.25 to +0.18	-1.08 to -0.04
Solid Rh	-0.56 to +0.06	-1.02 to -0.056
Solid Pd	+0.22 to +0.64	-0.88 to -0.07
Union Carbide Composite	-0.70 to +0.66	-1.04 to +0.03
Union Carbide Composite (Uncatalyzed)	---	-0.20 to 0.00

Temperature dependence studies on the pulsing effect of Union Carbide catalyzed composite anodes and cathodes were run at several temperatures ranging from 23 to 70°C. No significant temperature effect was noted.

A test to determine the effect of pulsing on electrode life was run with Union Carbide composite electrodes. Four cells were placed on continuous testing at 50 ma/cm<sup>2</sup> for 21 days. Two of the cells were pulsed twice daily. The average daily cell voltages over the 21-day test period for the pulsed cells were 0.830 and 0.823, respectively, and 0.762 and 0.802 for the control cells.

Potentiostatic scans on smooth Pt, Rh and Pd electrodes versus a Hg/HgO reference were conducted in O<sub>2</sub> and H<sub>2</sub> free 6 N KOH solutions. This was done to gain information about the oxidation states corresponding to the electrode potentials attained during the heavy discharge pulse. The results indicate that pulsing Pt and Rh anodes to potentials slightly more negative than would be associated with surface oxidation improves catalytic activity. It is necessary to pulse Pd anodes more intensely to the potential region associated with surface oxidation (Pd(OH)<sub>2</sub>) in order to improve catalytic activity.

Cathodic heavy discharge pulsing of Pt, Rh and Pd electrodes to a potential corresponding to an unoxidized surface state appears to improve catalytic activity for oxygen reduction.

### INTRODUCTION

In order to obtain long life and a high operating level from a fuel cell, the catalyst must maintain its effectiveness for extended periods of time. Since experimental evidence indicates that activity of some types of catalyst deteriorates with usage, the useful life and operating level of a fuel cell depends to a great extent on the rate of catalyst deterioration. For this reason, any technique or method of periodically restoring catalyst activity would be extremely useful in extending life and maintaining performance levels of fuel cells.

In the course of a recent survey<sup>1</sup> on the effect of mechanical and electrical pulsing in the performance of fuel cell electrodes it was observed that under certain conditions heavy discharge pulses significantly improved the sustained performance level of fuel cells. Preliminary results indicated that this "pulsing effect" was related to catalyst reactivation. Because of the great importance of catalyst reactivation in extending useful fuel cell life, it was decided to conduct

a detailed investigation of this pulsing effect. In this investigation, heavy discharge pulsing will be studied on six different types of electrodes—Union Carbide composite, porous nickel, Union Carbide baked carbon, smooth platinum, Raney nickel (Justi-type), and American Cyanamid electrodes.

The dependence of the pulsing effect on the nature and concentration of catalyst and on the temperature as well as the influence of pulsing on electrode life will also be investigated.

### MEETINGS AND CONFERENCES

G. E. Evans and M. L. Kronenberg of Union Carbide met with M. R. Unger and W. Aldred of NASA at Union Carbide's Parma Technical Center on 13 November 1964 to discuss the scope and program of the contract. It was agreed that the initial studies on smooth Pt, Pd and Rh electrodes to help define the pulsing effect were appropriate. It was also agreed that direct evidence of the beneficial effects of pulsing as determined by life testing was a useful approach to evaluating pulsing phenomena.

### FACTUAL DATA

#### Task I. - Definition of Effect.

##### A. Purpose and Scope.

The purpose of this Task is to obtain detailed experimental information about conditions under which heavy discharge pulsing shows a maximum beneficial effect.\* This information is to be obtained on solid platinum electrodes; Union Carbide thin, composite electrodes; and porous nickel electrodes.

##### B. Experimental Equipment and Procedures.

A block diagram of a special instrument which was designed to provide controlled discharge pulses is shown in Fig. 1. This instrument was described in an earlier report<sup>1</sup> but has been modified and now provides controlled heavy discharge pulses from 2 to 3600 ma from 0.2 to 5 seconds duration and steady-state currents from 2 to 1600 ma. The pulses can be applied manually or at controlled intervals ranging from 15 sec to 15 min. The instrument also permits the option of an open circuit of 1 or 2 seconds duration to follow the heavy pulse. The instrument also employs the principle of the Kordes-Marko interrupter<sup>2</sup>, thus enabling

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\* Beneficial pulsing refers to instances where polarization is reduced as a result of the heavy discharge pulse; i. e., polarization immediately before and after pulsing as compared at the same steady-state current.

resistance-free or resistance-included measurements to be made. Before this instrument was modified for low current measurements, a series of discharge pulsing measurements were made on solid metal electrodes using the simple circuit shown in Fig. 2. Here the heavy discharge current was applied manually to the cell by means of a low resistance bypass (switch S). This circuit was used only with solid metal electrodes in the low current range (1 - 10 ma) since a voltage gradient results from the electrolyte resistance and is included in the voltage measurements.

The cell used for obtaining pulsing information on solid metal electrodes is shown in Fig. 3. The ground glass joints and liquid seal outlets permit the cell to be run under a controlled atmosphere. Concentration polarization is minimized by stirring at a controlled rate by means of the magnetic stirrer shown, controlled by a Variac. For all the data contained in this report the electrolyte used was 6 N KOH and the reference electrode is Hg/HgO/6 N KOH which is +0.1 volt with respect to a normal hydrogen electrode (NHE).

The cell used for obtaining pulsing information on composite electrodes and metal electrodes is shown in Fig. 4. The circulating system was devised in our laboratory to simulate actual operating conditions experienced by fuel cell batteries. Because of the circulating electrolyte cells can be run in this system for several months with very little attention.

In general, the following procedure was used to obtain pulsing information on the various types of electrodes. The cell was run at a steady-state current prior to pulsing. The current density employed depended upon the nature of the electrode and operating conditions and was adjusted to a steady-state value sufficient to polarize the working electrode 25 mv or more. The cell was then pulsed and the potential of the working electrode with respect to a mercuric oxide reference electrode was noted before, during and after pulsing. The polarizations immediately before and after pulsing are compared at the same steady-state currents. Pulsing is regarded as having improved the electrode performance (beneficial pulsing) when the polarization is less immediately after pulsing than immediately before. Preliminary experiments indicated that the potential to which an electrode was driven during the heavy discharge pulse was one of the main factors in determining whether beneficial pulsing occurs. For this reason, the electrode potential attained during the discharge pulse is noted

as a measure of the pulse intensity. Since it is obvious that an electrode cannot improve indefinitely (e. g. , to negative polarizations) the condition of the electrode immediately before pulsing must also be a factor in determining whether the electrode performance will improve as a result of a single heavy discharge pulse. In addition it must be noted that driving an electrode to a given potential level means that the electrode has passed through a potential range while getting to that level and again when returning to its steady-state potential following the pulse. It cannot be readily established therefore whether an improved performance resulted from driving the electrode to the maximum polarization observed or to some intermediate polarization along the way.

### C. Experimental Results.

The range of potentials attained during heavy discharge pulsing according to the procedure described above was observed for solid Pt, Rh and Pd electrodes in both H<sub>2</sub> and O<sub>2</sub> saturated 6 N KOH solutions. The circuit shown in Fig. 2 was used and a Varian G-10 recorder was used to record electrode potentials. Typical data reproduced from a recorder tape (No. 601) are shown in Fig. 5 for a solid Pt electrode. Referring to Fig. 5 the following explanation is pertinent: at point "A" the Pt anode-reference potential (Hg/HgO) was -0.850 volt, but decayed to -0.743 volt (point "B") after 29 minutes. At point "B" a single pulse which drove the electrode to -0.19 volt (point "C") caused the electrode to improve to -0.805 volt (point "D"). During the next 23 minutes ("D" to "E") the potential deteriorated from -0.805 to -0.669 volt. A single pulse to -0.37 volt ("F") did not improve the electrode performance because the electrode recovered to only -0.658 ("G") after the pulse. However, the next pulse to -0.31 ("H") caused the electrode to improve to -0.695 ("I"). As shown in Fig. 5, successive pulses to -0.29, -0.25, -0.18, -0.11 and -0.02 volt all continued to improve the electrode to the final value shown here of -0.827 volt. Then the recorder scale was changed to zero center (not shown here) to accommodate even stronger pulses (positive values). The electrode continued to show improvement at positive values of pulsing up until +0.08 volt. The electrode did not recover at all when pulses drove the electrode beyond +0.08 volt. While later experiments showed that a Pt anode driven beyond +0.08 volt could be induced to recover by means of a short charging pulse, or by remaining at open circuit for several minutes, the data reported here refers to improvements resulting from a short discharge pulse followed by the immediate restoration of the normal current load.



The data obtained on solid Pt, Rh and Pd electrodes in the manner described above is summarized in Fig. 6. Here the metal electrodes were run as both H<sub>2</sub> anodes and O<sub>2</sub> cathodes. The potential range indicated in each instance (versus NHE) is the range to which an electrode has to be driven by a single heavy discharge pulse in order to recover to a lower polarization level immediately following the pulse. For example, referring to Figs. 5 and 6, pulsing an H<sub>2</sub>-Pt anode to -0.37 did not reduce its polarization upon recovery after the heavy discharge pulse, but pulsing the same electrode to -0.31 volt reduced the polarization by 37 mv ( $|0.695 - 0.658|$ ).

Potentiostatic scans on solid Pt, Rh and Pd electrodes versus an Hg/HgO reference were conducted in O<sub>2</sub> and H<sub>2</sub> free 6 N KOH solutions in both cathodic and anodic directions (Fig. 7 for Pd shown as an example). In the case of palladium two sets of conjugated peaks were identified ( $a_o$ ,  $a_r$ ,  $b_o$ ,  $b_r$ ) averaging 0.0 volt and +0.43 volt versus NHE in essential agreement with the results reported by Hickling and Vrjosek for N NaOH<sup>3</sup>. Based on data from Latimer<sup>4</sup>, Hickling attributed his 0.10 value to the Pd/Pd(OH)<sub>2</sub> couple and his 0.46 volt value to the Pd(OH)<sub>2</sub>/Pd(OH)<sub>4</sub> couple. Thus it appears, from the data presented in Fig. 6, that allowing for some concentration and ohmic polarization displacement during the high current pulse, the potential region associated with palladium catalyst reactivation corresponds more closely to Pd(OH)<sub>2</sub> than any other oxidation state. This is supported by the findings of Gray and co-workers<sup>5</sup> who recently reported that palladium and its alloys would chemisorb and adsorb hydrogen only after the potential necessary to form the first surface oxide was exceeded.

Despite the fact that a number of studies have been conducted on Pt oxidation states<sup>6-9</sup> and somewhat less on the oxidation states of Rh<sup>10,11</sup> the oxidation states existing in solution for both of these metals is still uncertain. For this reason the potentiostatic scanning results for Pt and Rh are difficult to interpret. However, there seems to be a general agreement that surface oxidation in alkaline solution occurs above approximately +0.15 volt for Pt and +0.4 volt for Rh versus NHE. Referring to Fig. 6, it appears that subjecting these metals to a potential where surface oxidation occurs reduces catalytic activity for hydrogen oxidation. Franke and co-workers<sup>12</sup> have already shown that on smooth platinum in acid solution the electro-oxidation of hydrogen decreases when the surface becomes oxidized. In the potential region just below surface

oxidation, however, where perhaps some form of oxygen chemisorption or intermediate oxidation state<sup>8</sup> occurs, the metals are reactivated.

Cathodic heavy discharge pulsing of the three metals to a potential corresponding to an unoxidized surface state appears to improve catalytic activity for oxygen reduction.

Pulsing experiments similar to those already described for smooth metal electrodes were run on Union Carbide composite electrodes. Anodic and cathodic pulses were applied by means of the resistance-free pulsing unit already described (see Fig. 1). The range of potentials (with respect to a NHE) which was observed for beneficial pulsing of these electrodes was -0.70 to +0.66 volt for anodes and -1.04 to +0.03 volt for cathodes. Beneficial pulsing for uncatalyzed, composite cathodes (uncatalyzed anodes will not run) was observed in the range 0.00 to -0.20 volt. The wide beneficial pulsing range for Union Carbide catalyzed anodes and cathodes was very encouraging. Also important was the observation that this mode of pulsing improved the operating level of normally working electrodes, although the maximum improvement resulting from a single pulse occurred on electrodes operating near their capacity limit.

Thus far only negative pulsing effects have been noted on Pt and Pt-Pd catalyzed, porous nickel electrodes. However, these electrodes were not run under proper operating conditions since they were designed to run at 7 psig gas pressure and could only support 1 psig due to imperfections in the porous structure. Properly operating porous nickel electrodes will be tested in pulsing experiments before any data on pulsing effects are reported.

#### Task II.- Catalyst Type.

The dependence of the pulsing effect on the nature and concentration of the catalyst is presently being determined on composite electrodes. The catalysts under investigation are Union Carbide, Pt, and Rh-Pd, using two levels of concentrations (1 and 3 mg/cm<sup>2</sup>). The tests have not been completed, but should be concluded before the end of the next reporting period.

#### Task III. - Temperature Effects.

Temperature dependence studies were conducted on Union Carbide catalyzed anodes and cathodes at three temperatures. The steady-state currents prior to pulsing were adjusted to permit pulsing effects at three different temperatures to

be compared at approximately the same voltage levels. In Table II are summarized representative results obtained on Union Carbide catalyzed, composite anode and cathodes.

TABLE II  
TEMPERATURE DEPENDENCE DATA USING CATALYZED ANODES AND CATHODES

Electrode Type	Temp. °C	Current Density (ma/cm <sup>2</sup> )	Potential vs. HgO			Improvement (mv) (After-Before)
			Before	During	After	
Anode	23	25	-.887	-.63	-.890	+3
Anode	40	45	-.887	-.67	-.888	+1
Anode	60	75	-.887	-.66	-.888	+1
Anode	23	25	-.890	-.52	-.898	+8
Anode	40	45	-.889	-.52	-.897	+8
Anode	60	75	-.890	-.64	-.892	+2
Anode	23	25	-.858	+.56	-.901	+43
Anode	40	45	-.860	-.69	-.891	+31
Anode	60	75	-.859	-.60	-.898	+39
Cathode	23	25	-.080	-.148	-.066	+14
Cathode	40	45	-.080	-.159	-.061	+19
Cathode	70	175	-.080	-.140	-.057	+23
Cathode	23	25	-.071	-.147	-.060	+11
Cathode	40	45	-.071	-.159	-.060	+10
Cathode	70	175	-.071	-.150	-.051	+20
Cathode	23	25	-.068	-.147	-.055	+13
Cathode	40	45	-.068	-.152	-.060	+8
Cathode	70	175	-.069	-.147	-.067	+2

For the three different pulsing conditions presented above, the anode improvements averaged +18 at 23°C; +13.3 at 40°C; and +14 mv at 60°C. Cathode improvements averaged +12.6 at 23°C; +12.3 at 40°C; and +15 mv at 70°C. Thus, no significant temperature effect was noted.

Temperature dependence studies on the pulsing effect is currently being investigated on smooth metal electrodes.

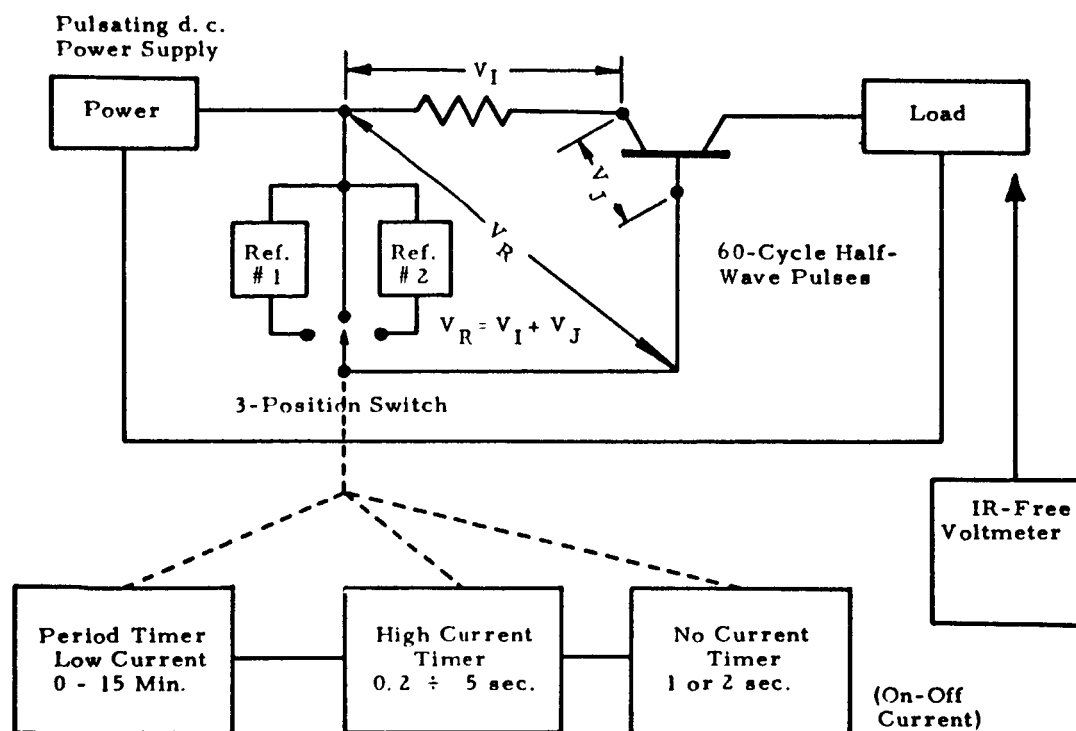
#### Task IV. - Life Testing.

On October 6, four Union Carbide composite electrode cells were placed on continuous testing in series at 50 ma/cm<sup>2</sup> and 50°C. Two of the four cells (here-

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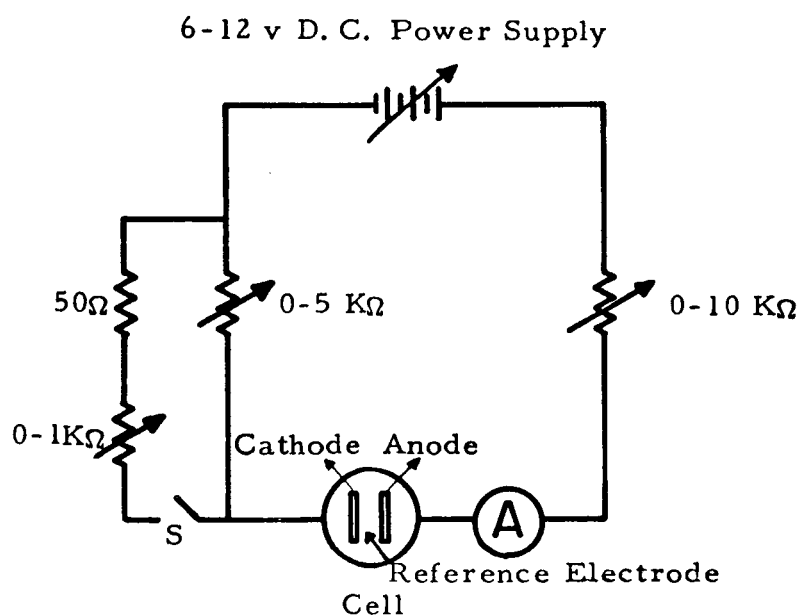
APPENDIX



Note: Ref. No. 1: Voltage control for low current range.  
Ref. No. 2: Voltage control for high current range.

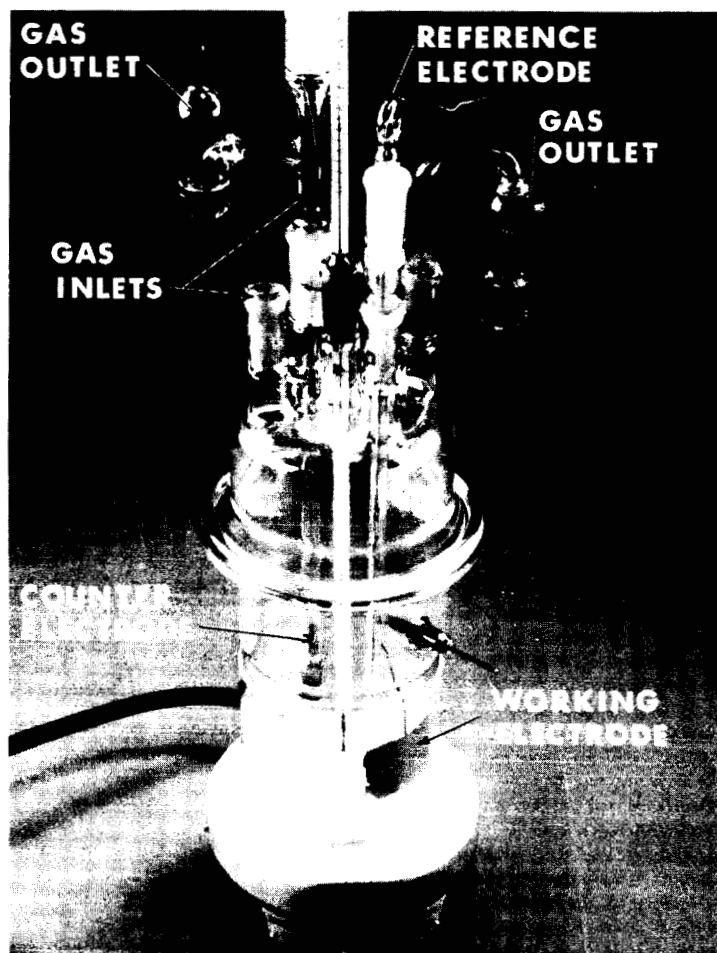
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Fig. 1 Dual Range Constant Current Interrupter. Timer Controlled.



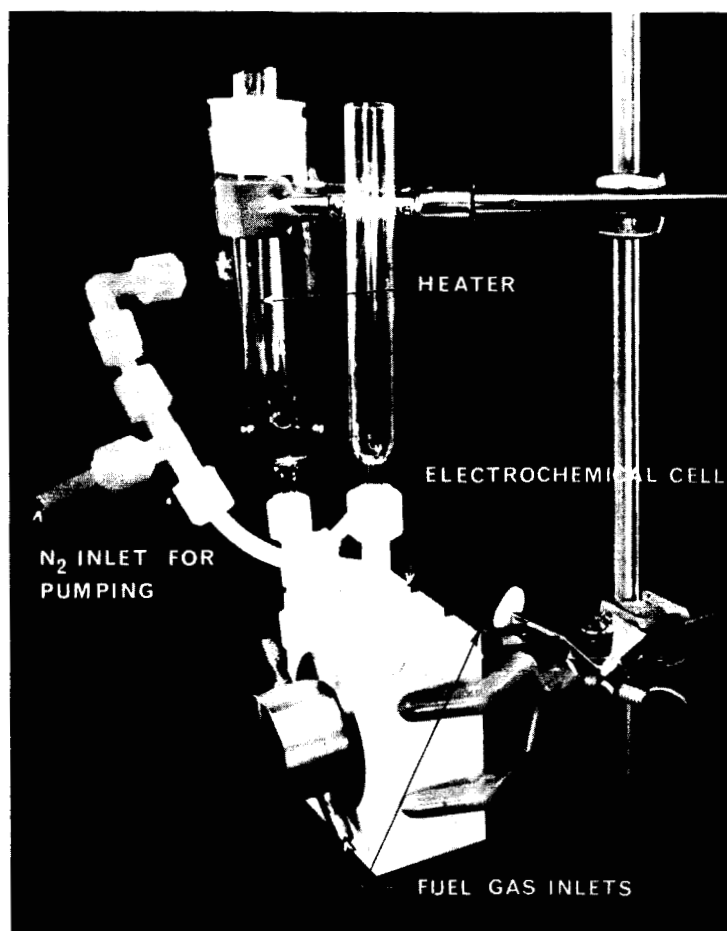
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Fig. 2 By-Pass for Heavy Discharge Pulsing.



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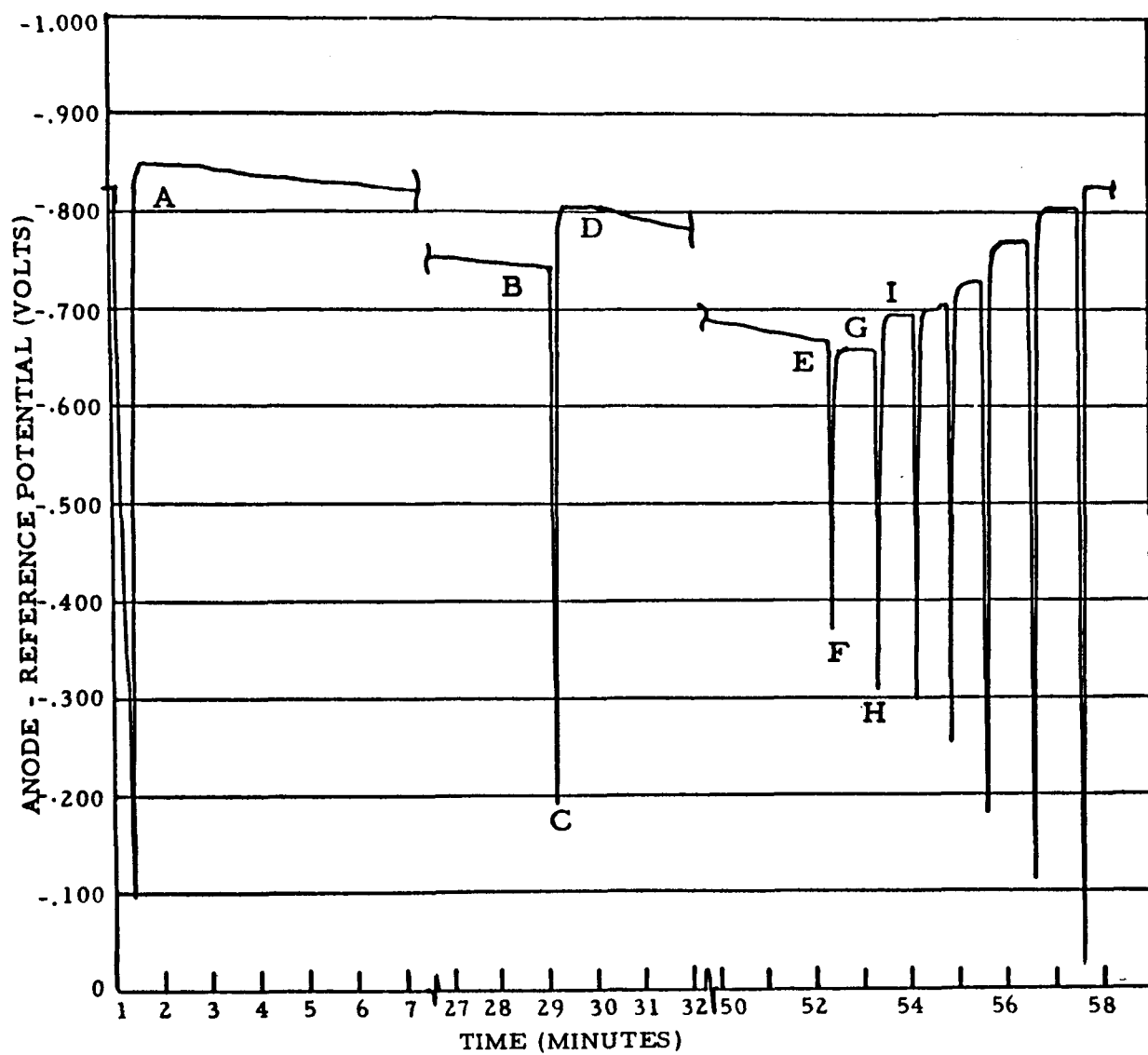
Fig. 3 Cell used to Obtain Information on Solid Electrodes.



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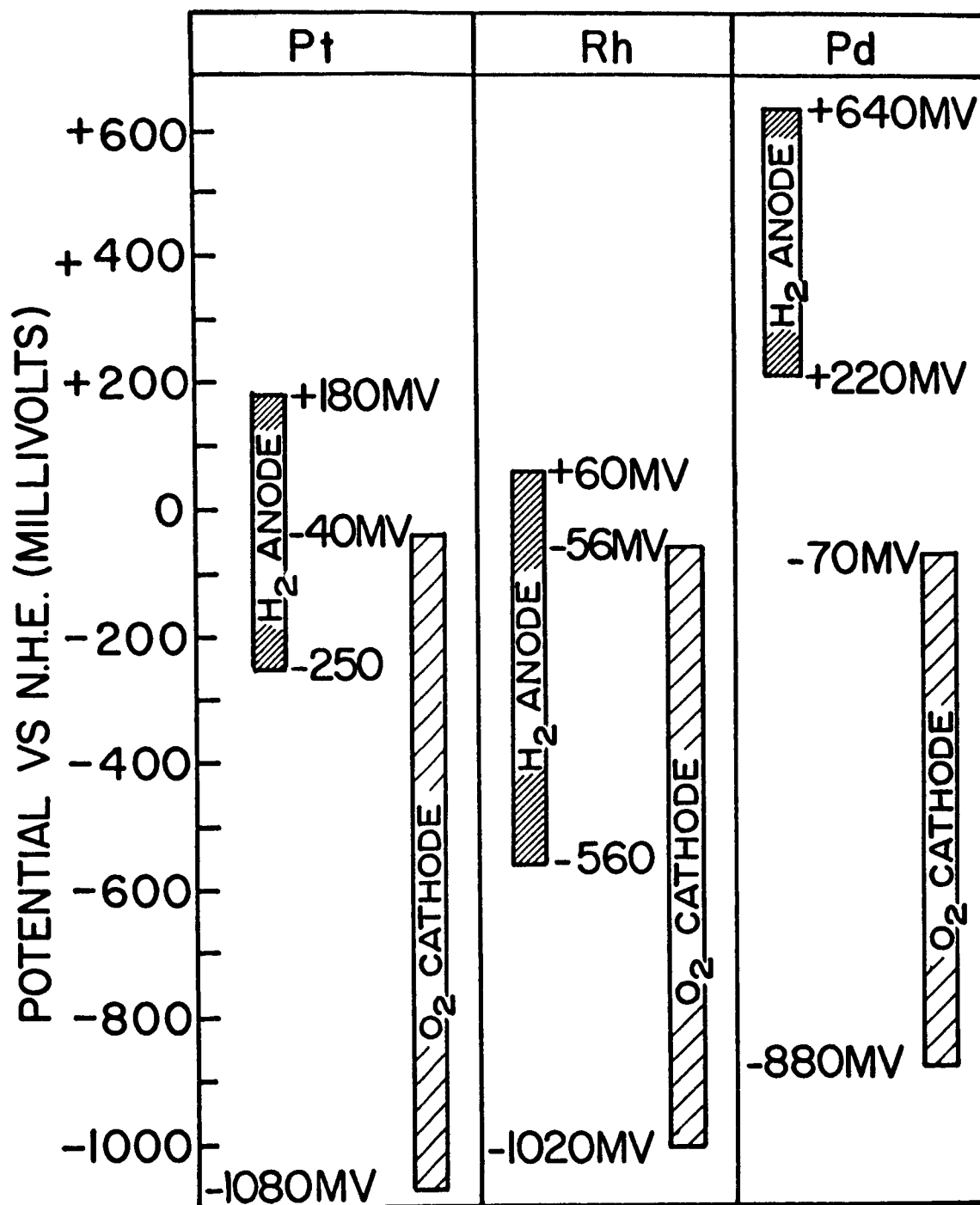
Fig. 4 Cell Used for Composite and Forous Metal Electrodes.





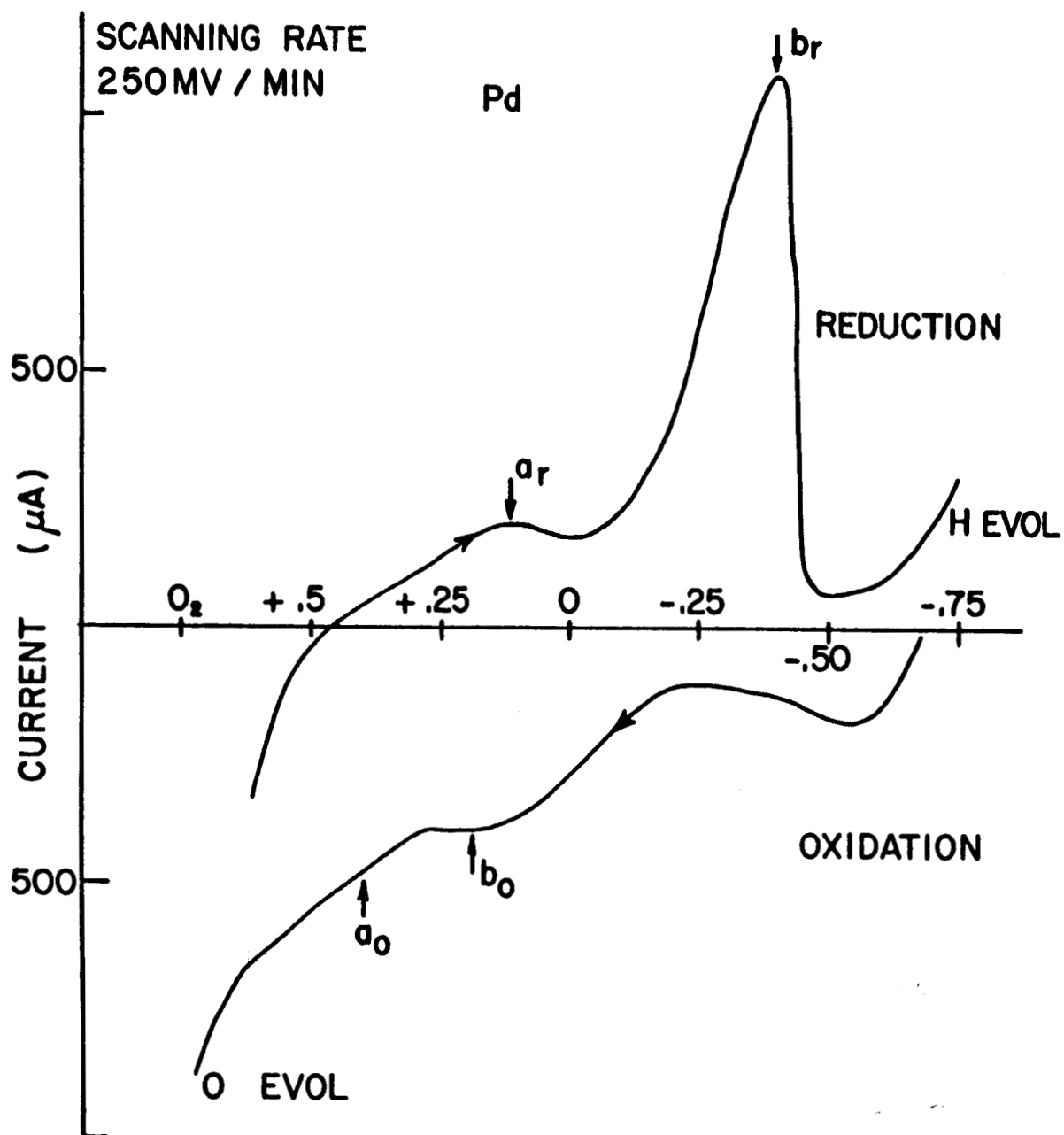
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Fig. 5 Recorder Tape of Anode-Reference Potential.



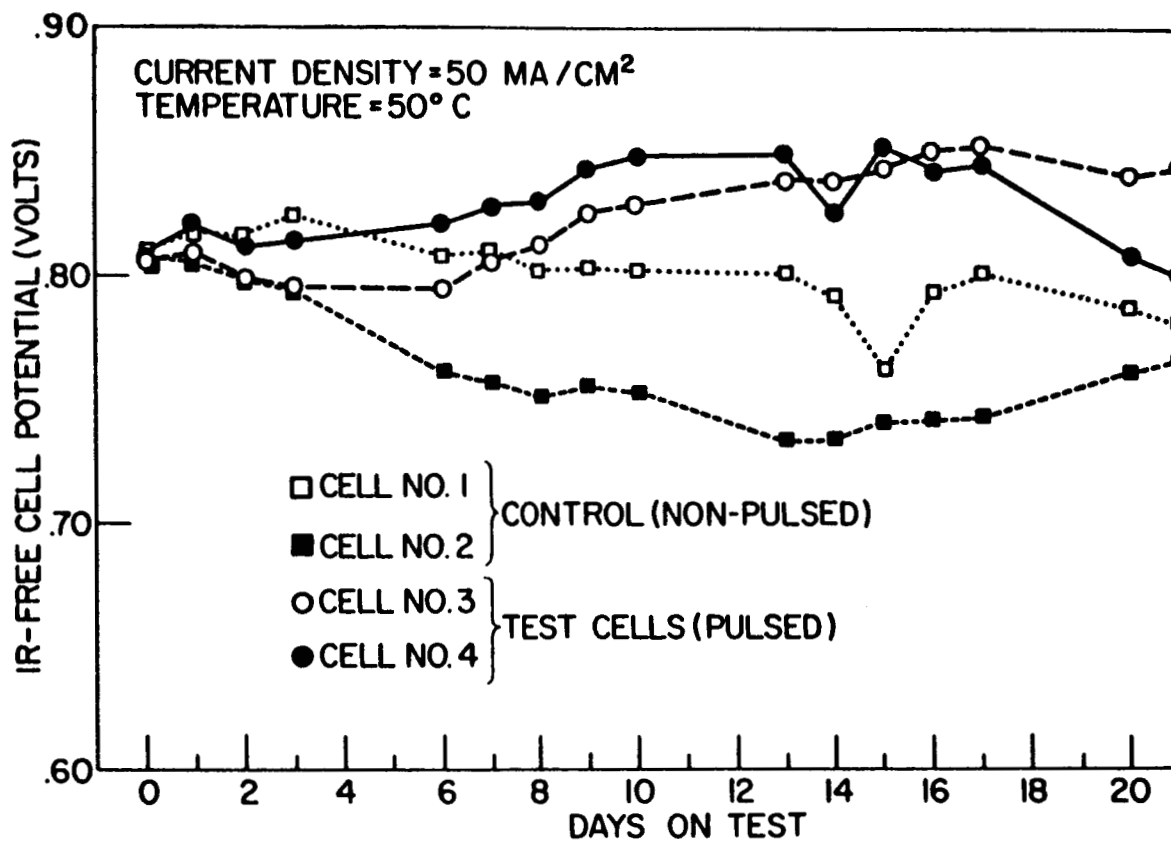
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Fig. 6 Range of Potentials for Beneficial Pulsing  
(Smooth Metal Electrodes).



D-1499

Fig. 7 Potentiostatic Scan of Pd Electrode vs. Hg/HgO  
in O<sub>2</sub> and H<sub>2</sub> Free 6 N KOH Solution.



D-1496

Fig. 8 Comparison of Cell Voltages for Pulsed and Non-Pulsed Union Carbide Composite Electrodes.